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The chromium isotopic composition of seawater and marine carbonates

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ABSTRACT

Chromium isotopes are fractionated during redox reactions and have the potential to provide a record of changes in the oxygenation levels of the oceans in the geological past. However, Cr is a trace metal in seawater and its low concentrations make isotopic measurements challenging. Here we report the first determinations of δ^{53}Cr for seawater from open ocean (Argentine Basin) and coastal (Southampton Water) settings, using a double-spike technique. The total chromium concentration in seawater from Southampton Water is 1.85 nM, whereas the Cr content of Argentine Basin samples is 5.8–6.6 nM. The δ^{53}Cr value of seawater from the Argentine Basin is 0.491–0.556‰ in intermediate and deep waters, and varies between 0.412 and 0.664‰ in surface waters (<150 m). The δ^{53}Cr value of Southampton Water seawater is 1.505‰, which may reflect *in situ* reduction of Cr(VI) to Cr(III). All of our seawater samples have higher δ^{53}Cr than crustal and mantle silicates, and mass balance modelling demonstrates that river water must also be enriched in heavy Cr isotopes, indicating that Cr isotopes are fractionated during weathering and/or during transport to the oceans.

We also show that the Cr isotopic composition of modern non-skeletal marine carbonates (0.640–0.745‰) encompasses the range that we measure for Argentine Basin seawater. Thus, fractionation of Cr isotopes during precipitation of these marine carbonates is likely to be small (<0.2‰), and they have the potential to provide a record of the Cr isotopic composition of ancient seawater. Phanerozoic carbonates are also characterised by heavy δ^{53}Cr and a correlation between δ^{53}Cr and Ce/Ce* suggests that the Cr and Ce cycles in the ocean are linked.

1. Introduction

Chromium is one of a number of trace metals, whose isotopic composition may provide important information about redox-controlled element cycling in the oceans (Anbar and Rouxel, 2007; Bullen and Eisenhauer, 2009). Although variations in the chromium concentration of seawater have attracted significant scientific interest for the past 40 years (e.g., Elderfield, 1970; Grimaud and Michard, 1974; Cranston and Murray, 1978; Jeandel and Minster, 1987; Connelly et al., 2006), Cr is present in concentrations of only a few nanomoles per litre (see Table 1 for compilation) so its distribution has been difficult to fully assess. Early research suggested that chromium was depleted in surface seawater, so Cr was assigned to the 'recycled' group of elements whose distribution in the oceans is similar to that of the nutrient elements, such as nitrate or phosphate (Whitfield and Turner, 1987). However, more recent studies indicate that the surface depletion is modest, and there is no substantial difference between Atlantic and Pacific deep-water concentrations (e.g. Sirinawin et al., 2000). Moreover, there is no correlation between Cr and the nutrient elements at the global scale (Sirinawin et al., 2000). For this reason, Cr is probably best described as intermediate between a 'conservative' and 'recycled' element, consistent with estimates of its residence time (8000–45,000 years: Campbell and Yeats, 1981; Broecker and Peng, 1982; Quinby-Hunt and Turekian, 1983; Whitfield and Turner, 1987).

In oxic seawater, the dominant chromium oxidation state is Cr(VI), which is consistent with thermodynamic calculations (Elderfield, 1970). However, significant amounts of Cr(III) have also been measured. The percentage of Cr(III) is usually <5% (e.g. Mugo and Orians, 1993), although some authors have found much higher quantities, sometimes accounting for over 90% of the total dissolved Cr (Connelly et al., 2006; Sander et al., 2003). It is generally accepted that the two Cr species display different behaviour in natural waters, with Cr(VI) being highly soluble in oxic waters, whereas Cr(III) is particle-reactive and forms insoluble chromium

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Table 1
Concentrations of Cr(VI) and total Cr (Cr(VI) + Cr(III)) measured in seawater and relatively pristine river waters.

	Reference	Cr(VI) (nM)	Total Cr (nM)
Ocean area			
NE Pacific Ocean	Cranston and Murray, 1978	1.6–3.5	
NE Pacific Ocean	Cranston, 1983		1.7–4.0
Eastern Pacific Ocean	Murray et al., 1983	1.1–6.0	
East Pacific Rise	Jeandel and Minster, 1984		1.9–15.8*
South Pacific Ocean	Golimowski et al., 1985		2.4
South and North Pacific Ocean	Jeandel and Minster, 1987		2.3–6.5
Pacific Ocean	Isshiki et al., 1989	2.1–4.2	2.9–4.6
Pacific Ocean	Sander et al., 2003	0.7–6.8	6.3-19.4†
North Pacific Ocean	Mugo and Orians, 1993	2.3–4.3	2.3–4.3
Indian Ocean	Ghaddaf, 1990	0.3–2.4	0.9–2.8
Mediterranean and Alboran Sea	Sherrell and Boyle, 1988		2.5–5.9
NW Mediterranean	Boussemart et al., 1992	4.5–5.8	
Mediterranean and Gibraltar	Achterberg and van den Berg, 1997	1.7–3.5	1.7–4.7
Atlantic Ocean near Gibraltar	Sherrell and Boyle, 1988		2.9–3.5
NW Atlantic Ocean	Campbell and Yeats, 1981		3.2–5.2
North Atlantic Ocean	Jeandel and Minster, 1987		2.0–4.6
North–South Atlantic Ocean	Sirinawin et al., 2000	3.1–7.3	
North Atlantic Ocean	Mugo and Orians, 1993		2.5–4.5
Arctic Ocean	Sirinawin et al., 2000	3.0–6.1	
Caribbean Sea	Sander et al., 2003	1.5-2.5	
Sargasso Sea	Connelly et al., 2006		2.5–6.5
Rivers			
Columbia river	Cranston and Murray, 1980	1.7–3.5	1.8–3.8
Humber estuary	Comber and Gardner, 2003	1.5–6.2	1.2–17.1
Sava river	Dragun et al., 2009		4.8–6.5
Orinoco river	Mora et al., 2009		1.4–11.3
Sacramento River	Taylor et al., 2012		1–7

* The sample with 15.8 nM Cr is thought to be affected by release of Cr from sediment pore fluids. All other samples have <3.7 nM Cr.
† Samples with high Cr(III) are thought to be affected by hydrothermal inputs.

hydroxide compounds (Cranston and Murray, 1978). While these differences can explain the low concentration and the relative proportions of Cr(VI) and Cr(III) in seawater, most Cr speciation calculations have been performed at Cr concentrations far higher than seawater. Fig. 1 shows the results of speciation calculations for seawater with a Cr concentration of 5 nM, with hydrolysis constants for Cr(III) hydroxides taken from Rai et al. (1987). These calculations confirm that Cr(III) hydroxide species are stable over a wide range of Eh and pH conditions (Fig. 1a), but at typical seawater Eh and pH values, chromate species dominate (Fig. 1b). The presence of dissolved Cr(III) in seawater is therefore inconsistent with speciation calculations, and is most probably due to sluggish oxidation of Cr(III) to Cr(VI) (Schroeder and Lee, 1975).

Isotopes of redox-sensitive metals have provided key information about past redox conditions at the Earth's surface. The most widely used elements are Fe (e.g. Rouxel et al., 2005) and Mo (Siebert et al., 2003; Archer and Vance, 2008; Duan et al., 2010; Voegelin et al., 2009). Cr also has the potential to provide constraints on redox conditions in the oceans and atmosphere because Cr isotopes are fractionated during redox reactions (Ellis et al., 2002), and a number of recent studies have attempted to use this system to trace changes in the level of O_2 in the atmosphere in the Archaean and Neoproterozoic (Frei et al., 2009; Frei et al., 2011; Frei et al., 2013). Nevertheless, before Cr isotope data can be fully interpreted, it is essential to properly ascertain the operation of the Cr cycle in Earth system processes.

Stable Cr isotope ratios are reported in standard delta notation relative to the SRM 979 Cr isotope standard:

$$\delta^{53}\mathrm{Cr} = \left(\frac{\frac{^{53}\mathrm{Cr}}{^{52}\mathrm{Cr}}\,\mathrm{sample}}{\frac{^{53}\mathrm{Cr}}{^{52}\mathrm{Cr}}\,\mathrm{NBS979}} - 1 \right) * 1000 \qquad (1)$$

The Cr isotopic composition of terrestrial silicates is relatively homogenous, with δ^{53}Cr values for the mantle and the continental crust ranging from −0.26‰ to −0.04‰ (Schoenberg et al., 2008). By contrast, groundwaters have higher δ^{53}Cr values, that range from 0.3 to 5.9‰ (Ellis et al., 2002; Izbicki et al., 2008). Low values are attributed to input of anthropogenic Cr, while high values appear to be characteristic of groundwater with low levels of oxygen. This is because reduction of Cr(VI) to Cr(III), which is favoured when oxygen levels are low, leaves the remaining Cr(VI) enriched in the heavy isotopes (Ellis et al., 2002; Ellis et al., 2004; Zink et al., 2010). Biotic reduction of Cr(VI) to Cr(III) has the same effect (Sikora et al., 2008). Water samples from fully oxic groundwater recharge areas have δ^{53}Cr values of 1.2–2.3‰. As oxidation of Cr(III) to Cr(VI) does not appear to fractionate Cr isotopes (Zink et al., 2010), these relatively high δ^{53}Cr values are attributed to fractionation on mineral surfaces during oxidative weathering (Izbicki et al., 2008). As a result of these groundwater studies, a number of authors have postulated that modern (oxic) seawater should have $\delta^{53}\mathrm{Cr} > 0‰$ (Izbicki et al., 2008; Frei et al., 2009), and analyses of seawater precipitates (marine carbonates and BIFs) support this idea (Bonnand et al., 2011; Frei et al., 2009). A recent study of highly weathered carbonates (Frei and Polat, 2013) and our own analyses indicate that weathering residues have low δ^{53}Cr values, which provides further evidence that weathering will produce isotopically heavy fluids which will ultimately be delivered to the oceans via rivers. Thus, the Cr isotopic composition of modern seawater has the potential to help constrain the sources of Cr to the ocean, provide mechanistic explanations for the distribution of Cr(VI) and Cr(III), and assess the controls on the availability of toxic Cr(VI). Moreover, information about past variations in seawater δ^{53}Cr could potentially be obtained from analyses of marine carbonates (Bonnand et al., 2011; Frei et al., 2011) but, as yet, little is known about the relationship between the Cr isotopic composition of seawater and carbonates.

To date, however, there have been no direct measurements of the Cr isotope composition of seawater. In order to fill this gap, a number of challenges need to be overcome. These include the